STUDIES ON ISOTHERMAL URETHANE POLYMERIZATION

REJI JOHN, E. T. THACHIL, P. RAVINDRAN, N. R. NEELAKANTAN, AND N. SUBRAMANIAN

Department of Chemical Engineering
Indian Institute of Technology
Madras-600036, India

Abstract

Polyurethane reaction between a new polyol and TDI under isothermal conditions was investigated. The progress of the reaction was monitored by following the viscosity as well as the monomer conversion. Viscosity variations were measured by means of a cone-and-plate viscometer while conversion was estimated by IR technique. An already reported empirical relationship between these two was verified. Stockmayer’s formula for weight average molecular weight of a linearly polycondensing system was used to find molecular weights at every stage of the reaction. The interdependence of viscosity and weight average molecular weight was confirmed, and the value of the index \( m \) was obtained.

INTRODUCTION

The important characteristics of reactive resin systems are degree of cure, molecular weight, and viscosity. Of these parameters, viscosity and conversion can be determined fairly easily, while direct determination of molecular weight is more difficult. In the case of polycondensation, all three are interconnected by both empirical and analytical relationships [1–3]. Empirical relationships are easy to apply in the case of isothermal reactions because the values of the empirical constants remain same throughout the experiment. Because of the relative ease with which conversion and viscosity are determined, it
is convenient to estimate the molecular weight by indirect means. Nonisothermal effects can be practically eliminated if the reaction is uncatalyzed and slow. We have attempted to study a new polyol/isocyanate system from this angle. A new polyester polyol developed by Indian Space Research Organization (ISRO) was used for these studies.

Dependence of viscosity on conversion and molecular weight has been investigated by Macosko et al. in the case of polyurethanes [4, 5]. Fox and Berry [6] also have suggested a relationship between weight average molecular weight and viscosity. Empirical equations connecting viscosity and degree of conversion for various polymerization reactions have been put forward by Malkin [7]. One can find weight average molecular weight from conversion data using Stockmayer's general formula [8] for polycondensation.

THEORY

Viscosity and monomer conversion are related to each other by the following equation (7):

$$\eta = K_c (1 - \beta)^{-\alpha}$$

where $\eta$ = viscosity, $\beta$ = degree of conversion, $\alpha$ = a temperature-dependent constant, and $K_c$ = a constant. From the viscosity and the conversion data one can evaluate the constants of the above equation for a particular temperature. This provides a means of following a reaction by viscosity measurement.

In our experiments at room temperature, we have employed an excess of isocyanate because of the need to accelerate the reaction to a reasonable speed in the absence of any catalyst. Under these conditions crosslinking reactions might occur to some extent. But on treating the reaction product (after 72 h) with benzene, complete dissolution was observed. Hence it can be inferred that the extent of crosslinking is negligible especially at the low temperature of the reaction (29 ± 0.5 °C). The final elastomeric product will be an isocyanate-terminated prepolymer whose molecular weight will be ideally suited for use as a millable polyurethane.

Stockmayer's [8] general polycondensation equation for finding the weight average molecular weight can be suitably modified for this case. In our experiments a stoichiometry of 1:1.5 was used between polyol and isocyanate. Further, the polyol functionality is known to be 1.7. When these are taken into account, the equation takes the form
where $\bar{M}_w = \text{the weight average molecular weight of the polymer formed; }$
$\bar{M}_{n_{\text{poly}}} = \text{the number average molecular weight of the polyl; }$ $\bar{M}_{n_{\text{iso}}} = \text{the molecular weight of TDI; } p_b = \text{isocynate conversion.}$
Weight average molecular weight and viscosity are related by the following equation [6]

$$\eta = K(T) \bar{M}_w^m$$

where $K(T) = \text{a temperature-dependent constant; } \bar{M}_w = \text{weight average molecular weight of the reactive system; } m = \text{a constant; } \eta = \text{viscosity (cP).}$

In the case of isothermal reaction $K(T)$ is a constant. This relationship has also been expressed as [4]:

$$\eta = A \, e^{D/RT} \left( \frac{\bar{M}_w}{\bar{M}_{w_0}} \right)^{(C/RT + S)}$$

where $A, S, D,$ and $C$ are empirical constants. We have preferred the former equation so as to get a value for $m$ from our experimental data. The constants $K(T)$ and $m$ are determined from a log $\eta$ vs. log $M_w$ plot.

The gel point of the reactive resin occurs when $M_w$ becomes infinitely large and this happens when [8]

$$(\beta_A \beta_B)_{gel} = (f_e - 1)^{-1} (g_e - 1)^{-1}$$

where

$$f_e = \frac{\sum_i f_i^2 A_i}{\sum_i f_i A_i}$$

$$g_e = \frac{\sum_j g_j^2 B_j}{\sum_j g_j B_j}$$

$\beta = \text{degree of conversion of isocyanate}$

$\beta_B = \text{degree of conversion of polyl}$

$\beta_A$ and $\beta_B$ are related by the equation $\beta_A f_A = \beta_B g_B$. This can be used to find conversion at gel point. The corresponding gel time can be found from conversion–time data.
EXPERIMENTAL

Materials
Uncatalyzed Am + Bn types liquid polyurethane reacting systems were used. Am was a castor oil-based polyester polyol developed by ISRO Trivandrum, India (a patented product used for solid rocket propellant binder). Hydroxyl plus carboxyl value of this polyol is 50, $M_n = 2000 \pm 300$, initial viscosity at 30°C was 1.4 Pa·s, secondary hydroxyl group content was about 90%, and average functionality was 1.7. Bn was toluene diisocyanate (TDI) supplied by Bayer A. G. Germany. This is a mixture of 2,4 and 2,6 isomers.

Equipment
A cone-and-plate Brookfield digital viscometer (Model DV 11) attached with a constant temperature bath and recorder was used to measure the viscosity change of the reaction. The Perkin-Elmer PE 983 IR spectrophotometer was used to study the conversion of isocyanate as the reaction progressed.

PROCEDURE
In polyurethane reactions, polyol usually contains absorbed moisture and small traces of other active components which may react with the diisocyanate. Hence some additional isocyanate may have to be included in a practical formulation to counteract this diluent effect on ideal stoichiometry [9]. We have seen that a reaction system with a stoichiometry of 1:1 failed to solidify even after a long period. For these reasons we chose an NCO index of 1.5 in our formulation. This made it possible to measure the reaction viscosity from the initial liquid reactants stage to the final solid elastomer in a reasonably short period. The absence of any catalyst ensured that the reaction was slow enough to eliminate any nonisothermal effect. The reactants were mixed at room temperature (29 ± .5°C) for about 5 min. In order to ensure identical sampling and mixing conditions all studies were initiated at this point of time from the same batch. Different runs were conducted along the same lines.

ESTIMATION OF CONVERSION

IR Spectroscopy
A Perkin-Elmer (model PE 983) spectrophotometer was employed to find conversion values. About 0.1 mL of the sample was used; 25 mm sodium chloride plate were used as windows. Hourly readings at room temperature were taken
by operating the instrument in repeated scanning mode. Peaks at 2270 cm\(^{-1}\) corresponding to the free isocyanate were observed. Possible change in thickness of the sample during polymerization was compensated by taking the ratio of absorbance of an inert reference group to that of NCO [10]. The reference peak was 2900 cm\(^{-1}\) corresponding to a CH\(_2\) group. The absorbances of this group after 1 h, 4 h, and 8 h were noted. There was virtually no variation among these values.

**Viscometry**

About 1 cc of the mixed sample was transferred to the plate of the cone-and-plate Brookfield viscometer. Isothermal conditions were maintained at room temperature by adjusting the thermostat. The small size of the sample and the slow reaction facilitated this. Studies made earlier showed that the shear-thinning effect was negligible [11]. Various shear rates from 1 (0.5 rpm) to 100 sec\(^{-1}\) (50 rpm) were applied in quick succession to check for shear thinning. It was found that the viscosity was independent of shear rates. Changes in viscosity were measured from liquid reactants (1.4 Pa\(\cdot\)s) to the final solid elastomer (1.6 \times 10^3 Pa\(\cdot\)s).

**RESULTS AND DISCUSSION**

Figure 1 gives the IR spectra of the reaction mixture at three stages, 1, 4, and 8 h after mixing. The progressive depletion of the isocyanate can be noticed from the absorbance peak at 2270 cm\(^{-1}\). The formation of the polyurethane is evidenced by the amide absorption at 1715 cm\(^{-1}\) and 1560 cm\(^{-1}\). Figure 2 shows change of isocyanate concentration with time estimated by IR absorption. After 8 h about 62% of the original isocyanate is seen to have reacted.

Figure 3 shows the viscosity variation of the reaction mixture with time. The curve shown corresponds to the case of 30°C. At an advanced stage of the reaction the viscosity is seen to go through a sudden fall and a sudden rise. This has not been reported by other workers to our best knowledge. More studies are needed before any explanation can be offered for this phenomenon.

In Fig. 4 the viscosity is plotted against concentration of isocyanate on log-log coordinates. The plot is found to be a straight line. The slope of this line is \(-a = 1.62\). The last two points of the plot are seen to be showing slight deviation from the general trend. It is possible that at higher conversions the dependence of viscosity on conversion may be deviating from the relationship given earlier.

Weight average molecular weights of the system at different stages of the reaction were calculated using Stockmayer's formula. The results are plotted
FIG. 1. IR spectra of the polyurethane reacting system: 1—after 1 h; 2—after 4 h; 3—after 8 h.
FIG. 2. Change of isocyanate concentration with time during the isothermal curing of polyol with TDI at 29 ± 0.5 °C.

in Fig. 5 against time. After 5 h it shows a slight deviation from the general trend (broken line). Figure 6 shows the dependence of the weight average molecular weight on conversion. The molecular weight is found to increase rapidly with conversion after a fractional conversion of 0.4.

Figure 7 is a log–log plot of viscosity against weight average molecular weight. The plot is a straight line of slope $m = 1.10$. For linear polycondensation $m$ is in the region of 1 and for network condensation it is about 3.4 [4]. Since $m = 1.10$ it can be concluded that crosslinking in this case is negligible. The relationship suggested by Fox and Berry is seen to be valid for this reaction.
FIG. 3. Viscosity variation of isothermal cure of polyol with TDI at 29 ± 0.5°C.

FIG. 4. Viscosity vs. isocyanate concentration for the reaction at 29 ± 0.5°C.
FIG. 5. Weight average molecular weight vs. time.

The gel point was estimated by making use of the formula suggested by Stockmayer. On substitution of $g_e$ and $f_e$ in Eq. (1), the gel point was determined as 0.95.

CONCLUSIONS

Both viscometry and IR spectroscopy can be employed to follow the course of this urethane reaction. The viscosity vs. conversion data show typical
polycondensation behavior, viscosity remaining low until high conversions. The interdependence of viscosity and conversion is borne out by a power relationship. The calculated weight average molecular weight was found to influence the viscosity in the manner proposed by Fox and Berry. Even an excess of isocyanate was found to lead to only negligible amounts of crosslinking when the reaction temperature was low.

**FIG. 6.** Weight average molecular weight vs. conversion.
FIG. 7. Log–log plot of viscosity vs. weight average molecular weight.

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REFERENCES


